

PATENT COOPERATION TREATY

REC'D 22 MAR 2005

WIPO

PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Article 36 and Rule 70)



Applicant's or agent's file reference P2002J113	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. PCT/EP 03/12885	International filing date (day/month/year) 18.11.2003	Priority date (day/month/year) 20.11.2002
International Patent Classification (IPC) or both national classification and IPC C07C51/00		
Applicant EXXONMOBIL RESEARCH AND ENGINEERING COMPANY		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

 These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
 - VI ☐ Certain documents cited
 - VII ☐ Certain defects in the international application
 - VIII ☐ Certain observations on the international application

Date of submission of the demand 19.05.2004	Date of completion of this report 21.03.2005
Name and mailing address of the International preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Zuurdeeg, B Telephone No. +31 70 340-4467 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/12885**

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, Pages

1-70 as originally filed

Claims, Numbers

1-38 received on 10.02.2005 with letter of 09.02.2005

Drawings, Sheets

1/7-7/7 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. **PCT/EP 03/12885**

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes: Claims	1-38
	No: Claims	
Inventive step (IS)	Yes: Claims	
	No: Claims	1-38
Industrial applicability (IA)	Yes: Claims	1-38
	No: Claims	

2. Citations and explanations

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/EP 03/12885

Re Item V

**Reasoned statement with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Reference is made to the following documents:
 - D1: WO 98/47618 A (EXXON RESEARCH ENGINEERING CO) 29 October 1998 (1998-10-29)
 - D2: US-A-3 761 428 (SUGIER ANDRÉ AND MIQUEL JEAN) 25 September 1973 (1973-09-25)
 - D3: US-A-2 889 287 (SCOTT JR JOHN W) 2 June 1959 (1959-06-02)
 - D4: ABOUL-GHEIT AHMED KADRY: "ROLE OF ADDITIVES IN THE IMPREGNATION OF PLATINUM AND RUTHENIUM ON ALUMINA CATALYSTS" JOURNAL OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY, vol. 29, no. 8, August 1979 (1979-08), pages 480-486, XP008028876 OXFORD, GB
 - D5: US-A-4 073 750 (YATES DAVID J C ET AL) 14 February 1978 (1978-02-14)
 - D6: US-A-5 319 129 (GUSTAFSON BRUCE L ET AL) 7 June 1994 (1994-06-07)
 - D7: US-A-4 431 574 (VASUDEVAN STRINIVASAN ET AL) 14 February 1984 (1984-02-14)
 - D8: US-B-6 284 9171 (BREITSCHIEDL BORIS ET AL) 4 September 2001 (2001-09-04)
2. The present application does not meet the requirements of Article 33(1) PCT.
 - 2.1 The subject-matter of independent claim 1 is novel in view of documents D2-D8, because none of the cited prior art documents discloses a process for hydrogenation of organic compounds using catalysts prepared by partial decomposition on the support of a complex of the catalytically active metal and a nitrogen containing compound selected from amino acids or amino alcohols, such that new vibration bands appear in the infra red spectrum between 2100-2200 cm⁻¹. In D2-D8, the metal complex either is fully decomposed or not decomposed at all.
 - 2.2 However, it is at present not possible to identify in the application documents evidence that the combination of features of independent claim 1 provides an unexpected technical effect. Examples 7 to 14 relate to measurements of the total

dispersion of ruthenium as a function of reduction temperature. Only example 4 relates to a process for hydrogenation of DINP, but use is made of catalysts which have not been prepared according to the invention (partial decomposition).

Hence, no unexpected technical effects have been convincingly shown in relation to the claimed hydrogenation process using the catalyst, which has been prepared via the partial decomposition.

Therefore, no inventive step could be recognised for the subject-matter of claims 1-38 and it does not fulfill the requirements of Article 33(3) PCT.

Certain defects in the international application

Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D2-D4 and D6-D8 is not mentioned in the description, nor are these documents identified therein.

The description is not in conformity with the claims as required by Rule 5.1(a)(iii) PCT.

The units "mesh", "psig" and "torr" employed on pages 33, 44, 55 and 57, and in table 1 are not additionally expressed in terms of the units stipulated by Rule 10.1(a) PCT.

Certain observations on the international application

The embodiments of the invention described in examples 2a, 2b, 3, 4, 8, 9, 19 and 20 and shown in figures 1, 2 do not fall within the scope of the claims. This inconsistency between the claims and the description leads to doubt concerning the matter for which protection is sought, thereby rendering the claims unclear, Article 6 PCT.

Terms "the whole contents of which are hereby incorporated by reference" and the like used on pages 27, 28, 31 and 32 should be deleted upon entry in the regional phase.

REPLACED BY
ART 34 AMN**CLAIMS**

1. A process for hydrogenating one or more organic compounds, which process comprises bringing the one or more organic compound into
5 contact, under hydrogenation conditions, with a source of hydrogen in the presence of a catalyst comprising one or more catalytically active metal sites located on a catalyst support and recovering the hydrogenation products, wherein at least one of the catalytically active metal sites has
10 been obtained via the decomposition on the support of an organic complex of the metal.
2. A process according to claim 1 wherein the organic compounds comprises one or more unsaturated organic compounds.
- 15 3. A process as claimed in claim 2 wherein the unsaturated organic compounds comprise one or more benzenepolycarboxylic acids or one or more derivatives thereof, or a mixture of one or more benzenepolycarboxylic acids with one or more derivatives thereof.
- 20 4. A process as claimed in claim 3 wherein the benzenepolycarboxylic acid is selected from the group consisting of phthalic acid, terephthalic acid, isophthalic acid, trimellitic acid, trimesic acid, hemimellitic acid and pyromellitic acid and mixtures of two or more thereof.
- 25 5. A process as claimed in claim 3 wherein the benzenepolycarboxylic acid derivatives are selected from the group consisting monoalkyl and dialkyl esters of phthalic acid, terephthalic acid and isophthalic acid, monoalkyl, dialkyl and trialkyl esters of trimellitic acid, trimesic acid and
30 hemimellitic acid, monoalkyl, dialkyl, trialkyl and tetraalkyl esters of pyromellitic acid, where the alkyl groups can be linear or branched and each have from 3 to 18 carbon atoms, anhydrides of phthalic acid,

REPLACED BY
ART 34 AMDT

trimellitic acid and hemimellitic acid, pyromellitic dianhydride and mixtures of two or more thereof.

- 5 6. A process as claimed in any one of the preceding claims wherein the process is carried out at a pressure of 25 to 300 bar.
7. A process as claimed in claim 6 wherein the process is carried out at a pressure of 50 to 220 bar.
- 10 8. A process as claimed in any one of the preceding claims wherein the total metal dispersion of the hydrogenation catalyst is 45% or more and the metal dispersion relating to a strongly chemisorbed component of the total metal dispersion is 20% or greater
- 15 9. A process for the manufacture of a hydrogenation catalyst which process comprises;
- a) preparing a support having one or more organic complexes of one or more catalytically active metals located thereon; and
- 20 b) decomposing the one or more of the organic metal complexes located thereon.
- 25 10. A process as claimed in any one of the preceding claims wherein the organic complex is partially decomposed.
11. A process as claimed in any one of claims 1 to 9 wherein the organic complex is fully decomposed.
- 30 12. A process as claimed in any one of the preceding claims wherein the decomposition is undertaken under hydrogen.

REPLACED BY
ART 34 AMDT

13. A process as claimed in any one of claims 1 to 11 wherein after decomposition the partially or fully decomposed organic complex is treated with a source of hydrogen.
- 5
14. A process as claimed in any one of the preceding claims wherein the organic complex is derived from one or more organic nitrogen containing compounds and one or more catalytically active metals.
- 10
15. A process as claimed in claim 14 the one or more organic nitrogen-containing compounds are amines.
16. A process according to claim 14 wherein at least one of the amines is an aliphatic amine.
- 15
17. A process as claimed in claim 16 wherein at least one of the aliphatic amine contains one or more hydroxyl groups.
18. A process as claimed in claim 17 wherein the amine comprises one or more amines having hydroxyalkyl groups.
- 20
19. A process as claimed in claim 18 wherein the hydroxyalkyl groups are C₁-C₅₀-hydroxyalkyl, preferably C₁-C₈-hydroxyalkyl, particularly preferably C₁-C₄-hydroxyalkyl groups.
- 25
20. A process as claimed in claim 19 wherein the hydroxyalkyl groups are selected from one or more of the following groups: hydroxymethyl, 1-hydroxyethyl, 2-hydroxyethyl, 1-hydroxy-n-propyl, 2-hydroxy-n-propyl, 3-hydroxy-n-propyl and 1-hydroxy-methyl-ethyl.
- 30

REPLACED BY
ART 34 AMDT

21. A process as claimed in claim 19 wherein the hydroxyalkyl group containing nitrogen compound comprises one or more mono-, di-, and tri-, substituted aliphatic hydroxyalkylamines.
- 5 22. A process as claimed in claim 21 wherein the hydroxyalkylamine comprises one or more of the following amines; methanolamine, di-methanolamine, tri-methanolamine, ethanolamine, di-ethanolamine, tri-ethanolamine, butanolamine, di-butanolamine, tri-butanolamine, propanolamine, di-propanolamine, and tri-propanolamine.
- 10 23. A process according to claim 14 wherein the organic nitrogen-containing compound is one or more amino acids.
24. A process as claimed in claim 23 wherein the amino acid is L-arginine.
- 15 25. A process as claimed in any one of the preceding claims wherein the decomposition is undertaken via calcination.
26. A process as claimed in claim 25 wherein the organic complex is partially decomposed and the calcination temperature is less than the temperature, as determined by TGA in air, at which total weight loss of the organic complex occurs.
- 20 27. A process as claimed in claim 26 wherein the calcination temperature is between 200 °C and the temperature at which total weight loss of the organic complex occurs.
- 25 28. A process as claimed in claim 25 wherein the organic complex is fully decomposed and the calcination temperature is at or above the temperature, as determined by TGA, at which total weight loss of the organic complex occurs.
- 30

REPLACED BY
ART 34 AMDT

29. A process as claimed in claim 28 wherein the calcination temperature is between the temperature at which total weight loss of the organic complex occurs and 1000°C.
- 5
30. A process as claimed in any one of claims 1 to 24 wherein the decomposition is undertaken via pyrolysis.
31. A process as claimed in claim 30 wherein the organic complex is partially decomposed and the pyrolysis temperature is less than the temperature, as determined by TGA in an inert atmosphere or hydrogen, at which total weight loss of the organic complex occurs.
- 10
32. A process as claimed in claim 31 wherein the pyrolysis temperature is between 200 °C and the temperature at which total weight loss of the organic complex occurs.
- 15
33. A process as claimed in claim 30 wherein the organic complex is fully decomposed and the pyrolysis temperature is at or above the temperature, as determined by TGA in an inert atmosphere or under hydrogen, at which total weight loss of the organic complex occurs.
- 20
34. A process as claimed in claim 31 wherein the pyrolysis temperature is between the temperature at which total weight loss of the organic complex occurs and 1000°C.
- 25
35. A hydrogenation catalyst comprising one or more catalytically active metals and one or more support materials wherein the total metal dispersion is 45% or more and the metal dispersion relating to a strongly chemisorbed component of the total metal dispersion is 20% or greater.
- 30

REPLACED BY
ART 34 AMDT

36. A hydrogenation catalyst as claimed in claim 35 wherein the total metal dispersion is 50% or more.
37. A hydrogenation catalyst as claimed in claim 36 wherein the metal dispersion relating to a strongly chemisorbed component of the total metal dispersion is 30% or greater.
38. A process or catalyst as claimed in any one of the preceding claims wherein the catalyst support comprises silica.
39. A process as claimed in claim 38 wherein the silica is amorphous.
40. A process or catalyst as claimed in any one of claims 1 to 39 wherein at least one of the support materials is one or more ordered mesoporous materials.
41. A process or catalyst as claimed in any one of claims 1 to 40 wherein at least one of the support materials is one or more materials that may be synthesized using amphiphilic compounds as directing agents.
42. A process or catalyst as claimed in claim 41 wherein one or more of the ordered mesoporous materials is selected from the group consisting of materials designated as SBA (Santa Barbara) such as SBA-2, SBA-15 and SBA-16, materials designated as FSM (Folding Sheet Mechanism) such as FSM-16 and KSW-2, materials designated as MSU (Michigan State) such as MSU-S and MSU-X, materials designated as TMS or Transition Metal Sieves, materials designated as FMMS or Functionalised Monolayers on Mesoporous Supports or materials designated as APM or Acid Prepared Mesostructure or ordered mesoporous materials designated as M41S.

REPLACED BY
ART 34 AMDT

43. A process as claimed in claim 42 wherein the one or more ordered mesoporous materials designated as M41S are selected from the group consisting of MCM-41, MCM-48 and MCM-50.
- 5 44. A process as claimed in claim 43 wherein the ordered mesoporous material is MCM-41.
- 10 45. A process or catalyst as claimed in any one of the preceding claims wherein the catalyst support comprises one or more macroporous materials.
- 15 46. A process or catalyst as claimed in any one of the preceding claims wherein the catalyst support comprises one or more mixed porosity materials.
- 20 47. A process or catalyst as claimed in claim 46 wherein the mixed porosity material contains mesopores and macropores.
- 25 48. A process or catalyst as claimed in any one of the preceding claims wherein the one or more catalytically active metals are one or more metals selected from transition group VIII of the Periodic Table.
- 30 49. A process or catalyst as claimed in any one of the preceding claims wherein the one or more catalytically active metals includes a metal selected from the group consisting of platinum, rhodium, palladium, cobalt, nickel or ruthenium or a mixture of two or more thereof.
50. A process or catalyst as claimed in claim 49 wherein the one or more catalytically active metals are selected from the group consisting of platinum, palladium, ruthenium, nickel or a mixture of two or more thereof.

**REPLACED BY
ART 34 AMDT**

51. A process or catalyst as claimed in claim 50 wherein the catalytically active metal is ruthenium or nickel.

5 52. A process as claimed in any one of the preceding claims wherein one or more of the catalytically active metals comprises one or more metals of transition group Ib or VIIb or group VIIIb of the Periodic Table.

10